

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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PCT/NL 00 / 00404  
International Application No.

13 JUN 2000 (13.06.00)  
International Filing Date

BUREAU VOOR DE INDUSTRIËLE EIGENDOM  
P.C.T. INTERNATIONAL APPLICATION  
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum) P48815PC00

Box No. I TITLE OF INVENTION

Method for removing nitrogen oxides from an oxygen-containing gas stream

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

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☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

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## Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

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This person is:

- ☐ applicant only
- ☐ applicant and inventor
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**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

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**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)


<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 11 June 1999	1012296	NL		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s) 1

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

<b>Box No. VII INTERNATIONAL SEARCHING AUTHORITY</b>			
<b>Choice of International Searching Authority (ISA)</b> (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		<b>Request to use results of earlier search; reference to that search</b> (if an earlier search has been carried out by or requested from the International Searching Authority):	
ISA / EP		Date (day/month/year)	Number Country (or regional Office)
		13 January 2000	SN 33446 NL NL

<b>Box No. VIII CHECK LIST; LANGUAGE OF FILING</b>	
This international application contains the following number of sheets: request : 4 description (excluding sequence listing part) : 12 claims : 3 abstract : 1 drawings : sequence listing part of description : <b>Total number of sheets : 20</b>	This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify):
Figure of the drawings which should accompany the abstract:	Language of filing of the international application: English

<b>Box No. IX SIGNATURE OF APPLICANT OR AGENT</b>	
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).	
 <b>M. J. Hatzmann</b>	

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1. Date of actual receipt of the purported international application:	13 JUN 2000	
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VO P48815PC00

Titel: Werkwijze voor het verwijderen van stikstofoxiden uit een zuurstofhoudende gasstroom

De uitvinding heeft betrekking op de katalytische omzetting van stikstofoxiden in moleculaire stikstof, welke stikstofoxiden gevormd worden bij verbranding van koolwaterstoffen en/of synthesegas ( $H_2/CO$ ). Meer in het bijzonder heeft zij betrekking op het omzetten van stikstofoxiden in  
5 aanwezigheid van zuurstof zoals deze bijvoorbeeld gevormd worden bij het bedrijven van eenheden zoals verbrandingsmotoren onder zogenaamde arme of 'lean-burn' condities, dat wil zeggen: onder verbrandingscondities waarbij een overmaat zuurstof aanwezig is. De uitvinding heeft verder betrekking op het omzetten van stikstofoxiden welke bij industriële processen, zoals  
10 salpeterzuurproductie, gevormd kunnen worden.

Bij de verbranding van koolwaterstoffen met moleculaire zuurstof (bijvoorbeeld afkomstig uit lucht) kunnen door de heersende temperatuur en druk tijdens het verbrandingsproces oxiden van stikstof ontstaan. Deze-  
stikstofoxiden, waaronder NO en  $NO_2$ , (gewoonlijk aangeduid met  $NO_x$ ),  
15 zijn zeer belastend voor het milieu. Stikstofoxiden worden onder meer verantwoordelijk gehouden voor de vorming van zure regen en fotochemische smog.

Verschillende werkwijzen voor het terugdringen van  $NO_x$ -uitstoot zijn bekend en een aantal daarvan wordt reeds in de praktijk toegepast.

20 Het terugbrengen van  $NO_x$ -uitstoot wordt bij stoechiometrisch draaiende motoren vaak bewerkstelligd door gebruik te maken van een zogenaamd driewegkatalysatorsysteem. De  $NO_x$ -omzettingskatalysator in dergelijke systemen is in staat om stikstofoxiden om te zetten in onschadelijke verbindingen door het met de in het uitlaatgas aanwezige  
25 reducerende verbrandingsproducten zoals koolwaterstoffen en CO te laten reageren tot  $N_2$ .

Over het algemeen zijn de bekende drie-wegkatalysatoren die de reductie van stikstofoxiden bewerkstelligen niet in staat om deze omzetting uit te voeren in de aanwezigheid van een aanzienlijke hoeveelheid zuurstof.

30 Dit is met name een probleem bij het verwijderen van stikstofoxiden uit de uitlaatgassen van genoemde, onder arme condities werkende motoren, zoals onder arme condities werkende gasturbines,

dieselmotoren, gasmotoren en afgassen van industriële processen, aangezien in dergelijke gassen, naast stikstofoxiden een aanzienlijke hoeveelheid zuurstof aanwezig is. Bovendien zijn koolwaterstoffen en/of CO niet of in onvoldoende mate aanwezig, hetgeen succesvol bedrijven van de  
5 bovengenoemde driewegkatalysatorsystemen in de weg staat.

In installaties waar een aanzienlijke hoeveelheid zuurstof in het uitlaatgas aanwezig is, wordt daarom vaak een hoeveelheid reductant toegevoegd. De stikstofoxiden kunnen dan door de reductant in aanwezigheid van een geschikte katalysator (DeNOx-katalysator) worden  
10 omgezet. Deze werkwijze staat bekend als zogenaamde Selectieve Katalytische Reductie ('Selective Catalytic Reduction', SCR).

Veel gebruikte reductanten voor de SCR-reactie zijn ammoniak en ureum. Ook is het uit de literatuur bekend om koolwaterstoffen zoals etheen, propaan en propaan als reductant te gebruiken (zie bijvoorbeeld  
15 G.P. Ansell *et al.*, 'Mechanism of the lean NOx reaction over Cu/ZSM-5', Appl. Catal. B, 2 (1993), pp. 81-100). Andere mogelijke reductanten zijn bijvoorbeeld CO, H<sub>2</sub> en CH<sub>4</sub>, ethanol, koolwaterstoffen, in het bijzonder brandstoffen zoals benzine en dieselolie.

Verreweg het meest gebruikt als reductant in praktische SCR-toepassingen zijn echter ammoniak of ureum, danwel een waterige ureumoplossing. Het gebruik van deze middelen brengt een aantal nadelen met zich mee. De dosering is uiterst kritisch. Indien een te grote hoeveelheid ammoniak of ureum bij de deNOx-katalysator wordt ingebracht,  
20 (dat wil zeggen: meer dan nodig is voor het omzetten van de stikstofoxiden) zal dit leiden tot zogenaamde ammoniakslip. De uitstoot van ammoniak uit dergelijke installaties is zo mogelijk nog schadelijker uit milieuoogpunt dan die van NOx. Ook is het mogelijk dat door oxidatie van ammoniak deze overdosering juist leidt tot de productie van NOx, hetgeen haaks staat op het beoogde doel, namelijk het terugbrengen van de NOx-uitstoot. Een  
30 ander nadeel van het gebruik van ammoniak of ureum is de benodigde opslag ervan en de noodzaak om de voorraad periodiek aan te vullen indien dit niet binnen battery limits geproduceerd wordt. Met name ammoniak is zeer gevaarlijk en schadelijk en het vervoer ervan brengt grote veiligheids- en milieurisico's met zich mee. Dit alles maakt dat zowel de  
35 investeringskosten als de operationele kosten van deze techniek hoog zijn.

Hoewel de keuze voor andere reductiemiddelen, zoals bijvoorbeeld de hierboven genoemde koolwaterstoffen, deze problemen gedeeltelijk zouden kunnen oplossen, blijven er nog steeds nadelen bestaan, zoals de noodzaak tot apart transport en opslag. De daarmee gepaard gaande risico's voor veiligheid en milieu zijn vaak niet acceptabel.

Het gebruik van dezelfde brandstof die in de motor, de (gas)turbine of het verbrandingsproces wordt gebruikt of aanwezig is bij industriële processen als reductiemiddel, zou dit probleem oplossen. De koolwaterstoffen die in bijvoorbeeld dieselolie en benzine aanwezig zijn blijken echter niet voldoende actief om onder procescondities met een aanvaardbare snelheid en selectiviteit NOx om te zetten.

Het is bekend om uit te gaan van een SCR-katalysator waarbij het benodigde reductiemiddel wordt vervaardigd uit een voorhanden zijnde koolwaterstofbron zoals methanol, LPG en aardgas, eventueel onder toevoeging van H<sub>2</sub> dat is verkregen uit elektrolyse of dat is opgeslagen in voorraadtanks.

In DE-A-44 04 617 wordt een techniek beschreven waarbij met behulp van een elektrisch verwarmde reactor een koolwaterstof bevattende brandstof katalytisch wordt gekraakt bij 200 tot 700 °C en de kraakproducten met lucht verder worden geactiveerd voordat ze als reductiemiddel aan het uitlaatgas worden toegevoegd, waarna de totale gasstroom over een SCR-katalysator wordt geleid.

Volgens DE-A-196 00 558 worden ook gekraakte koolwaterstoffen toegepast als reductiemiddel. Deze koolwaterstoffen zijn verkregen uit diesel. Volgens deze bekende werkwijze wordt onder SCR-condities waterstof aan het uitlaatgas toegevoegd om NOx over de SCR-katalysator te reduceren waar de gekraakte koolwaterstoffen niet voldoende actief zijn. De waterstof is afkomstig van een voorraadtank of wordt gemaakt door middel van elektrolyse of methanolreforming.

De toevoeging van waterstof als reductiemiddel voor de reductie van NOx in de uitlaatgassen van continue verbrandingsprocessen staat beschreven in DE-A-42 30 408. Ook hier kan de waterstof verkregen worden door elektrolyse of uit het reformen door middel van steamreforming of partiële oxidatie (PO) van koolwaterstof bevattende brandstof. Om een waterstofstroom met zo min mogelijk koolmonoxide te verkrijgen worden

twee shift-reactoren achter de reformer geplaatst om de CO met waterdamp voor het grootste gedeelte om te zetten in waterstof en CO<sub>2</sub>.

Het gebruik van ter plaatse gemaakte waterstof als reductiemiddel voor de reductie van NO<sub>x</sub> uit uitlaatgas van interne verbrandingsmotoren staat beschreven in EP-A-0 537 968. Hierin wordt de techniek van reforming (steamreforming en partiële oxidatie) van koolwaterstof bevattende brandstoffen beschreven. De condities dienen volgens deze publicatie zo te worden gekozen, dat de hoeveelheid CO in de waterstof zo laag is, dat de CO-concentratie geen problemen ten aanzien van emissies kan opleveren. De voor de reforming benodigde temperatuur wordt bereikt door gebruik te maken van de warmte van de uitlaatgassen. De reductie van NO<sub>x</sub> wordt uitgevoerd over een SCR-katalysator. Als oxidatiemiddel voor de partiële oxidatie wordt lucht genoemd.

Volgens de onderhavige uitvinding worden in een reductantvormende stap koolwaterstoffen omgezet in een reductantenstroom onder geschikte condities, eventueel door deze in contact te brengen met een reductantvormende katalysator. De koolwaterstoffen in de productstroom van de reductantvormende stap kunnen ongereageerde koolwaterstoffen uit de voeding van deze stap zijn, maar kunnen ook kleinere koolwaterstoffen zijn die gevormd zijn door kraakreacties tijdens de reductantvormende stap.

De reductanten kunnen door toepassing van een reductantvormende katalysator worden bereid uit bijvoorbeeld resten koolwaterstoffen die zich in het uitlaatgas van de eenheid waarin de verbranding plaatsvindt, bevinden. Ook is het mogelijk om deze koolwaterstoffen te betrekken uit een andere bron, bijvoorbeeld de brandstof voor de verbrandingseenheid die reeds ter plaatse beschikbaar is. Combinaties van effluent en een dergelijke andere bron zijn uiteraard ook mogelijk. De voor deze stap benodigde zuurstof is althans gedeeltelijk afkomstig uit het te behandelen afgas, dat wil zeggen het stikstofoxide- en zuurstofhoudende gas. Bij voorkeur wordt in hoofdzaak alle zuurstof aanwezig in het voor de reductantvorming gebruikte deel van het afgas gebruikt voor de vorming van de reducerende gasstroom. De in dit gedeelte van het afgas aanwezige koolwaterstoffen kunnen tevens in deze stap worden omgezet tot reducerende verbindingen. De in het afgas aanwezige

koolwaterstoffen kunnen dan tevens in deze stap worden omgezet tot reducerende verbindingen.

Door toepassing van een geschikt reductantvormend proces, desgewenst met gebruikmaking van een katalysator, kunnen de voor de  
5 katalytische reductie van NOx noodzakelijke reductanten in de vorm van CO en/of H<sub>2</sub>, optioneel aangevuld met koolwaterstoffen, ter plaatse worden bereid uit koolwaterstoffen, waardoor bovengeschetste bezwaren in het verwijderen van NOx onder zuurstofrijke condities althans gedeeltelijk kunnen worden opgeheven.

10 Naast de genoemde reductanten, CO en/of H<sub>2</sub>, optioneel aangevuld met koolwaterstoffen, kan in aanwezigheid van waterstof en stikstof, onder geschikte procescondities ook ammoniak (NH<sub>3</sub>) gevormd worden vanwege de ligging van het chemische evenwicht  $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$ . Ammoniak is zoals hierboven vermeld een goede reductant.

15 Het gebruik van een deel van de uitlaatgassen als bron van koolwaterstoffen en zeker als oxidatiebron voor de (katalytische) partiële oxidatie en/of steamreforming heeft als groot voordeel ten opzichte van de bestaande technologie dat de emissie van onverbrande koolwaterstoffen  
20 uitlaatgasstroom daalt waardoor de condities voor de NOx-en verbeteren en de energie aanwezig in de vorm van warmte in de uitlaatgassen direct voor het katalytische proces gebruikt kan worden zonder gebruik te maken van extra warmtewisselend oppervlak.

Een ander voordeel is dat geen zuiver H<sub>2</sub> of H<sub>2</sub> met kleine  
25 hoeveelheden koolmonoxide hoeft te worden geproduceerd. Hierdoor is het mogelijk om shiftreactoren en membraantechnologie achterwege te laten.

De reductantvormende stap kan een partiële-oxidatiestap zijn, waarbij gebruik kan worden gemaakt van een partiële-oxidatiekatalysator. Daarnaast is het mogelijk om zonder katalysator de partiële oxidatie uit te  
30 voeren, bijvoorbeeld door aan een brandstofstroom een gecontroleerde hoeveelheid energie toe te voeren, bijvoorbeeld door middel van een elektrische ontlading. Ook kan de reductantvormende stap een stoomreformeringsstap zijn waarbij gebruik gemaakt wordt van een stoomreformeringskatalysator. Een combinatie van partiële oxidatie en  
35 stoomreforming is ook mogelijk.

Een geschikte reductantvormende katalysator is bijvoorbeeld een partiële-oxidatiekatalysator. In aanwezigheid van een dergelijke katalysator vindt de partiële oxidatie van koolwaterstoffen plaats. De voor deze partiële oxidatie benodigde zuurstof wordt zoals vermeld volgens de  
5 uitvinding betrokken uit het effluent van de verbrandingseenheid, eventueel aangevuld met van elders betrokken zuurstof, welke bijvoorbeeld afkomstig is uit toegevoegde lucht. De productstroom van de partiële-oxidatiestap is zeer geschikt om als reductantenstroom te worden toegepast.

Een andere mogelijkheid om een stroom die  $H_2$  en/of  $CO$ , en  
10 optioneel koolwaterstoffen omvat te bereiden uit een stroom die koolwaterstoffen omvat, is door een zogenaamde stoomreforming toe te passen. Naast koolwaterstoffen dient bij stoomreforming water aan de stoomreformeringsstap te worden toegevoegd. Dit water kan afkomstig zijn uit het effluent van de verbrandingsmotor, uit een aparte voorraad of uit  
15 een combinatie van deze twee bronnen. Bij stoomreforming worden koolwaterstoffen omgezet met water (stoom) tot een mengsel van koolwaterstoffen, zoals methaan, en/of  $H_2$  en  $CO_2$ . Als gevolg van chemische evenwichten kan naast deze componenten ook  $CO$  aanwezig zijn. Het op deze wijze ontstane mengsel is zeer geschikt om als reductantenstroom te  
20 worden toegepast.

Vervolgens worden de reductantstroom tezamen met het effluent van de verbrandingseenheid in contact gebracht met een de $NO_x$ -katalysator waardoor de gewenste omzetting van stikstofoxiden plaatsvindt.

Het ter plaatse produceren van de reductant biedt een aantal  
25 belangrijke voordelen. Zo kan de aanvoer van reductanten volgens de uitvinding continu geschieden, in geval van aardgas, of in elk geval tegelijk met de aanvoer van de brandstof voor de verbrandingseenheid en is het niet meer nodig om deze apart op voorraad te hebben en te houden. Dit kan bijvoorbeeld praktisch zijn bij toepassing in mobiele verbrandingseenheden,  
30 zoals vracht- of personenauto's omdat dan geen aparte opslagtanks aanwezig hoeven te zijn voor het reductiemiddel. Ook bij stationaire eenheden kan dit een belangrijk voordeel zijn. Ook is het feit dat geen ammoniak en ureum (al dan niet als ureumoplossing) wordt gebruikt, althans niet extern betrokken hoeft te worden, een voordeel, omdat de

bovengeschetste nadelen die aan het gebruik van deze reductanten kleven zich niet meer voordoen.

Een ander voordeel van de uitvinding doet zich voor indien koolwaterstoffen uit het effluent van de verbrandingseenheid worden  
5 gebruikt als voeding voor de reductantvormende stap, waardoor dan de hoeveelheden koolwaterstoffen in het uitlaatgas omlaag zullen worden gebracht, doordat deze gebruikt worden voor de reactie met NO<sub>x</sub>. Een dergelijke vermindering is gunstig, aangezien de uitstoot van koolwaterstoffen vanuit milieuoogpunt ongewenst is. Een ander voordeel  
10 van het gebruik van het effluent van de verbrandingseenheid voor de vorming van het reducerende gas is de vermindering van de voor de reductantvorming benodigde hoeveelheid koolwaterstoffen.

Derhalve wordt de onderhavige uitvinding gekenmerkt door een werkwijze voor het terugbrengen van het gehalte aan stikstofoxiden in een  
15 stikstofoxide- en zuurstofhoudende gasstroom door deze gasstroom in aanwezigheid van een deNO<sub>x</sub>-katalysator in contact te brengen met een reducerende gasstroom, welke CO, H<sub>2</sub> en eventueel NH<sub>3</sub> omvat en welke reducerende gasstroom is verkregen door koolwaterstoffen om te zetten met de zuurstof uit genoemde stikstofoxide- en zuurstofhoudende gasstroom,  
20 desgewenst in aanwezigheid van een reductantvormende katalysator.

Volgens een voorkeursuitvoering is genoemde stikstofoxide- en zuurstofhoudende gasstroom het effluent van een stap voor het verbranden van brandstoffen, welke de stappen omvat van het toevoeren van tenminste een stroom a) omvattende één of meer brandstoffen en een ten opzichte van  
25 de brandstof overmaat zuurstof bevattende stroom b) welke verder stikstof omvat, waarbij genoemd effluent tezamen met genoemde reducerende gasstroom c) die verder optioneel één of meer koolwaterstoffen omvat, met genoemde deNO<sub>x</sub>-katalysator in contact wordt gebracht, waarbij aan stroom c) geen ammoniak en geen ureum wordt toegevoegd en waarbij stroom c) in  
30 hoofdzaak verkregen is door het in contact brengen van stromen d) en e) met genoemde reductantvormende katalysator, waarbij stroom d) één of meer koolwaterstoffen omvat en stroom e) zuurstof en water omvat.

De verbrandingseenheid is geschikt voor de opwekking van warmte, en optioneel van arbeid. De verbrandingseenheid kan op basis van  
35 een vlam werken maar de verbranding in de verbrandingseenheid kan ook

langs katalytische weg verlopen. Bij voorkeur is de verbrandingseenheid een gasmotor, gasturbine, dieselmotor of benzinemotor.

Met een stroom c) die in hoofdzaak vrij is van extern toegevoegd ammoniak en ureum wordt bedoeld dat er aan deze stroom volgens de  
5 uitvinding geen reductanten van dit type hoeven te worden toegevoegd. Wel kunnen er ammoniak, en eventueel daarvan afgeleide verbindingen zoals ureum, aanwezig zijn, als gevolg van de bovengenoemde evenwichtsreactie van  $N_2$  en  $H_2$ .

De  $NO_x$  wordt volgens onderhavige uitvinding gereduceerd met een  
10 mengsel van  $H_2$ , CO en eventueel  $NH_3$ . Daarnaast kunnen nog niet (geheel) omgezette koolwaterstoffen in de reducerende gasstroom aanwezig zijn. Ook deze koolwaterstoffen werken als reductant. Het reducerende gasmengsel wordt verkregen door de koolwaterstoffen uit een deel van de  
15 uitlaatgasstroom met eventueel extra toegevoegde koolwaterstoffen om te zetten door middel van (katalytische) partiële oxidatie, stoomreforming of een combinatie van beide technologieën met behulp van de zuurstof en waterdamp aanwezig in hetzelfde deel van de uitlaatgasstroom en eventueel extern toegevoegde lucht en/of waterdamp. Eventueel kan aan het  
20 verkregen reducerende gasmengsel extra reductiemiddel worden toegevoegd zoals waterstof.

Bijzondere voorkeur heeft de werkwijze en de daartoe geschikte inrichting volgens de uitvinding waarbij de motor voorzien is van een warmtewisselaar, zodanig dat ten minste een gedeelte van de bij de  
25 verbranding vrijkomende warmte nuttig kan worden aangewend, bijvoorbeeld voor verwarming, zoals van kassen of andere ruimten. Dergelijke eenheden, waarbij tezelfdertijd zowel warmte als arbeid worden opgewekt, waarbij de arbeid veelal in de vorm van elektrisch vermogen is, worden ook wel warmte-krachteenheden of warmte-krachtcentrales genoemd.

30 Ook kan de uitvinding worden toegepast in diverse vervoermiddelen zoals vaartuigen, vliegtuigen, vracht- en personenauto's en treinen voorzien van een op koolwaterstoffen gestookte locomotief.

De werkwijze volgens de uitvinding en de daartoe geschikte inrichtingen is met name geschikt voor het bedrijven van  
35 verbrandingseenheden onder zogenaamde lean-burncondities, dat wil

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zeggen: condities waarbij de verhouding tussen de stromen a) en b) zodanig  
gekozen is dat de hoeveelheid zuurstof ten minste de voor de volledige  
verbranding van de brandstoffen in stroom a) benodigde hoeveelheid is. Dit  
zijn de omstandigheden waaronder zuurstof in het effluent van de  
5 verbrandingseenheid aanwezig is en waarbij met voordeel de deNO<sub>x</sub>-reactie  
met het effluent van de katalytische partiële oxidatie-stap kan worden  
uitgevoerd.

Geschikte brandstoffen voor de voedingsstroom a) zijn  
koolwaterstoffen en/of synthesegas (CO/H<sub>2</sub>-mengsel).

10 Bij voorkeur worden de koolwaterstoffen voor de  
reductantvormende stap althans gedeeltelijk betrokken uit dezelfde bron als  
de brandstof voor de verbrandingseenheid. In dit geval omvatten stroom a)  
en stroom d) dezelfde componenten.

15 Teneinde het gehalte koolwaterstoffen in de uitstoot van de  
inrichting voor de werkwijze volgens de uitvinding terug te brengen, worden  
de koolwaterstoffen die aanwezig zijn in het effluent van de  
verbrandingseenheid althans gedeeltelijk toegepast als voeding voor de  
reductantvormende stap, al dan niet aangevuld met een  
koolwaterstoffenstroom die van elders wordt betrokken.

20 Teneinde het zuurstofgehalte bij het in contact brengen van de  
stromen met de deNO<sub>x</sub>-katalysator laag te houden, wordt het effluent van  
de verbrandingseenheid toegepast als zuurstofbron, al dan niet aangevuld  
met een zuurstofstroom die van elders wordt betrokken.

25 Als brandstof voor de verbrandingseenheid en/of als voeding voor  
de reductantvormende stap kunnen naast synthesegas in principe alle  
daartoe geschikte koolwaterstoffen worden aangewend. Praktische voorkeur  
geniet het echter, wanneer de koolwaterstoffen uit stroom a) en d)  
onafhankelijk gekozen zijn uit de groep bestaande uit aardgas (dat in  
hoofdzaak methaan omvat), methaan, dieselolie, benzine, stookolie,  
30 methanol, ethanol, nafta, kerosine, ethaan, propaan, butaan, LPG,  
derivaten en mengsels daarvan.

De katalysator voor het omzetten van stikstofoxiden kan worden  
gekozen uit de groep katalysatoren die de reductie van NO<sub>x</sub> katalyseren,  
zoals de gangbare katalysatoren voor verwijdering van NO<sub>x</sub>. Bij voorkeur  
35 worden deze gekozen uit de groep omvattende zeolieten, metaalgewisselde

zeolieten, zoals met Co, Cu en/of Ce gewisselde zeolieten, Pt, Rh en/of Ir katalysator, desgewenst aangebracht op een drager zoals een washcoat welke verder Ba, La, Y, Sr, Pr, Ce, Si, Ti, Al en/of Zr kan omvatten.

5 De katalysator voor de partiële oxidatie van koolwaterstoffen kan worden gekozen uit de groep bestaande uit Pt, Rh, Ru, Pd, Co en Ni, desgewenst aangebracht op geschikte dragers zoals  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , silica/alumina-zeolieten en mengsels daarvan, eventueel gestabiliseerd met bijvoorbeeld Si, La, Ba of Y en mengsels daarvan.

10 De stoomreformeringskatalysator die in staat is om een mengsel van koolwaterstoffen en water om te zetten in een mengsel van  $\text{H}_2$ , CO,  $\text{CO}_2$  en/of koolwaterstoffen kan iedere gebruikelijke stoomreformeringskatalysator zijn, al dan niet op een drager, volgens gebruikelijke technieken, zoals bij de vakman bekend. Bij voorkeur is de stoomreformeringskatalysator een gedragen katalysator die Ni, Rh en/of Pt  
15 omvat.

Voor het bedrijven van een inrichting volgens de uitvinding dienen factoren als koolwaterstof/zuurstof-verhouding, temperatuur, druk, verblijftijd en/of hoeveelheid katalysator voor de partiële oxidatie van koolwaterstoffen zodanig gekozen te worden dat er geen volledige oxidatie  
20 plaatsvindt. De molaire koolwaterstof/zuurstof-verhouding wordt uitgedrukt in  $\lambda_{\text{PO}}$ , zodanig dat voor stoechiometrische verhoudingen (dat wil zeggen: juist voldoende zuurstof om de volledige verbranding van de brandstof te bewerkstelligen) geldt dat  $\lambda_{\text{PO}} = 1$ . Volgens de uitvinding dient  $\lambda_{\text{PO}} < 1$  te zijn. Bij voorkeur geldt dat  $0,2 < \lambda_{\text{PO}} < 0,7$ .  $\lambda_{\text{PO}}$  is regelbaar door instelling  
25 van de lucht/brandstof-hoeveelheid en is afhankelijk van de gebruikte koolwaterstoffen.

De temperatuur voor de reductantvormende stap ligt in het algemeen tussen 250 en 1100°C. De verblijftijd voor de reductantvormende stap ligt in het algemeen tussen 200 en 150.000  $\text{h}^{-1}$ . Hoewel de druk ook van  
30 invloed zal zijn, wordt deze over het algemeen opgelegd door de overige procescondities. In het algemeen zal de druk atmosferisch of iets hoger zijn en niet hoger zijn dan 50 bar.

Het gebruik van een SCR-katalysator als methode om  $\text{NO}_x$  met een reductiemiddel om te zetten in  $\text{N}_2$  heeft veelal de beperking dat in een  
35 beperkt temperatuurvenster voldoende omzetting van  $\text{NO}_x$  kan worden

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bereikt. Zo wordt in DE-A-196 00 558 als praktisch voorbeeld een conversiecurve van  $\text{NO}_x$  als functie van de temperatuur gegeven, waarin een conversie van 40% wordt bereikt. Dit is typisch voor SCR-systemen die niet met  $\text{NH}_3$  of ureum werken als reductiemiddel. Het zodanig kiezen van de  
5 procescondities van de reductantvormende stap, dat ook  $\text{NH}_3$  wordt gegenereerd is dus van voordeel omdat dan een hogere  $\text{NO}_x$ -conversie kan worden bereikt.

Wanneer een hoge conversie van  $\text{NO}_x$  vereist is, zoals bijvoorbeeld bij toepassing van uitlaatgassen als bemestingsgas in de tuinbouw, kan de  
10 werkwijze volgens de onderhavige uitvinding in plaats van met een SCR-systeem beter met een  $\text{NO}_x$ -opslagsysteem worden uitgevoerd. Indien de de $\text{NO}_x$ -stap wordt uitgevoerd met een dergelijk  $\text{NO}_x$ -opslagsysteem (ook wel  $\text{NO}_x$  Storage and Reduction Catalyst, NSR genoemd), zoals bijvoorbeeld beschreven in N. Takhashi et al., Environmental Catalysis, blz. 45, (1995)  
15 kan een zeer hoge conversie in  $\text{NO}_x$  worden verkregen. Volgens deze werkwijze laat men stikstofoxiden uit de stikstofoxide- en zuurstofhoudende gasstroom absorberen aan een geschikt absorbens en brengt men vervolgens, bijvoorbeeld door te schakelen, genoemde reducerende gasstroom in contact met genoemd absorbens. De de $\text{NO}_x$ -stap wordt zo  
20 discontinu bedreven. Een zeer effectieve  $\text{NO}_x$ -verwijdering kan zo verkregen worden.

Met dit  $\text{NO}_x$ -opslagsysteem is het mogelijk om in een oxiderend milieu ( $\lambda > 1$ )  $\text{NO}_x$  te absorberen en in een reducerend milieu ( $\lambda < 1$ ) zowel het  $\text{NO}_x$  in het uitlaatgas als het geadsorbeerde  $\text{NO}_x$  om te zetten naar  
25 stikstof. De katalysator in het  $\text{NO}_x$ -opslagsysteem kan zeer geschikt uit platina aangebracht op een bariumbevattende en/of zeolietomvattende alumina washcoat bestaan. Het aanwezige barium kan reageren met  $\text{NO}_x$  tot bariumnitraat. Dit nitraatzout ontleedt in een reducerend milieu tot barium en  $\text{N}_2$ .

30 Het  $\text{NO}_x$ -opslagsysteem kan volgens de uitvinding worden bedreven door de uitlaatgassen door het  $\text{NO}_x$ -opslagsysteem te leiden totdat het systeem verzadigd is met  $\text{NO}_x$ . Vervolgens kan geregenereerd worden met een reductiemiddel dat verkregen is als hierboven beschreven. Eventueel kan dit reductiemiddel worden aangevuld met een extern  
35 betrokken reductiemiddel.

Bij voorkeur wordt dit NOx-opslagsysteem met minimaal twee parallelle bedden uitgevoerd. Hierbij wordt een bed toegepast om NOx te absorberen, terwijl het andere bed wordt geregenereerd. Zodra het eerstgenoemde bed verzadigd is en/of het tweede bed voldoende  
5 geregenereerd, wordt er geschakeld met de stromen waardoor het geregenereerde bed NOx kan gaan absorberen en het beladen NOx-bed wordt geregenereerd doordat de geabsorbeerde NOx wordt omgezet in stikstof.

Het effluent van de regeneratiestap van het NOx-opslagbed kan  
10 met voordeel worden gerecirculeerd en tezamen met de inlaatlucht naar de inlaat van de verbrandingseenheid (bijvoorbeeld een gasmotor) worden geleid. Dit biedt ten minste twee voordelen. In de eerste plaats hoeft op deze wijze geen CO-houdend gas gespuid te worden. In de tweede plaats is het volgens deze uitvoeringsvorm van minder belang om een volledige  
15 omzetting van koolwaterstoffen tot CO/H<sub>2</sub> te krijgen in de voorafgaande bereidingsstap van de reducerende gasstroom.

Zowel de deNOx-katalysator als de reductantvormende katalysator kunnen bij de werkwijze volgens de uitvinding aanwezig zijn in de bij de vakman bekende vormen zoals in de vorm van een bed van korrels,  
20 extrudaten, granules, en/of pellets, danwel aangebracht op keramische of zogenaamde metalen monolieten, of anderszins gestructureerde vormen.

De toepassing van de katalysator in gestructureerde vorm verdient de voorkeur omdat hiermee overige voor de werkwijze van belang zijnde factoren, zoals drukval, menging, contacttijd, warmtehuishouding,  
25 mechanische sterkte en levensduur, door geschikte keuzen op de heersende condities kunnen worden afgestemd en daarmee de werkwijze kan worden geoptimaliseerd.

De uitvinding wordt dus gekenmerkt door het gebruik van een katalysator geschikt voor het omzetten van stikstofoxiden in combinatie met  
30 ofwel een katalysator geschikt voor de partiële oxidatie van koolwaterstoffen, ofwel een katalysator geschikt voor stoomreforming, voor het omzetten van stikstofoxiden bij het opwekken van warmte en optioneel arbeid uit koolwaterstoffen, zonder dat daarbij ammoniak of ureum extern hoeven te worden toegevoegd.

## CONCLUSIES

1.       Werkwijze voor het terugbrengen van het gehalte aan stikstofoxiden in een stikstofoxide- en zuurstofhoudende gasstroom door deze gasstroom in aanwezigheid van een deNOx-katalysator in contact te brengen met een reducerende gasstroom, welke CO, H<sub>2</sub> en eventueel NH<sub>3</sub>  
5       omvat en welke reducerende gasstroom is verkregen door koolwaterstoffen om te zetten met zuurstof en/of water uit genoemde stikstofoxide- en zuurstofhoudende gasstroom desgewenst in aanwezigheid van een reductantvormende katalysator.
2.       Werkwijze volgens conclusie 1, waarbij in hoofdzaak alle in het  
10       voor de reductantvorming gebruikte deel van genoemde stikstofoxide- en zuurstofhoudende gasstroom aanwezige zuurstof wordt verbruikt.
3.       Werkwijze volgens een der voorgaande conclusies, waarbij genoemde stikstofoxide- en zuurstofhoudende gasstroom het effluent is van een stap voor het verbranden van brandstoffen, welke de stappen omvat van  
15       het toevoeren van tenminste een stroom a) omvattende één of meer brandstoffen en een ten opzichte van de brandstof overmaat zuurstof bevattende stroom b), waarbij genoemd effluent tezamen met genoemde reducerende gasstroom c) die verder optioneel één of meer koolwaterstoffen omvat, met genoemde deNOx-katalysator in contact wordt gebracht, waarbij  
20       aan stroom c) geen ammoniak en geen ureum wordt toegevoegd en waarbij stroom c) in hoofdzaak verkregen is door het onderwerpen van stromen d) en e) aan een reductantvormende stap, waarbij stroom d) één of meer koolwaterstoffen omvat.
4.       Werkwijze volgens een der voorgaande conclusies, waarbij  
25       genoemde stikstofoxide- en zuurstofhoudende gasstroom afkomstig is uit een warmte-krachteenheid.
5.       Werkwijze volgens een der voorgaande conclusies, waarbij genoemde reducerende gasstroom wordt verkregen door een partiële-oxidatiestap, gebruikmakend van een partiële-oxidatiekatalysator, dan wel

een stoomreformeringsstap, gebruikmakend van een stoomreformeringskatalysator uit te voeren.

6.       Werkwijze volgens een der conclusies 3-5, waarbij de brandstof in stroom a) synthesegas en/of één of meer koolwaterstoffen omvat.
- 5   7.       Werkwijze volgens een der conclusies 3-6, waarbij stroom a) en stroom d) althans gedeeltelijk dezelfde verbindingen omvatten.
8.       Werkwijze volgens een der conclusies 3-7, waarbij de brandstof in stroom a) koolwaterstoffen omvat welke, evenals de koolwaterstoffen in stroom d), onafhankelijk gekozen zijn uit de groep bestaande uit aardgas,  
10   methaan, dieselolie, benzine, stookolie, methanol, ethanol, nafta, kerosine, ethaan, propaan, butaan, LPG en mengsels daarvan.
9.       Werkwijze volgens een der voorgaande conclusies, waarbij een reductantvormende katalysator wordt toegepast welke een partiële-oxidatiekatalysator voor de partiële oxidatie van koolwaterstoffen is, gekozen uit de  
15   groep bestaande uit Pt, Rh, Ru, Pd, Co en Ni en combinaties daarvan, optioneel aangebracht op een drager welke drager optioneel gestabiliseerd is met Si, La, Ba en/of Y.
10.      Werkwijze volgens een der voorgaande conclusies, waarbij de reductantvormende katalysator een stoomreformeringskatalysator is die Ni,  
20   Rh en/of Pt omvat.
11.      Werkwijze volgens een der voorgaande conclusies, waarbij de reductantvormende stap een partiële-oxidatiestap is, waarbij de verhouding koolwaterstoffen en zuurstof zodanig gekozen is dat er geen volledige oxidatie plaatsvindt.
- 25   12.      Werkwijze volgens een der voorgaande conclusies, waarbij men stikstofoxiden uit de stikstofoxide- en zuurstofhoudende gasstroom laat absorberen aan een geschikt absorbens en vervolgens genoemde reducerende gasstroom in contact brengt met genoemd absorbens.

13. Werkwijze volgens conclusie 12, waarbij genoemd absorbens een barium- en/of zeolietomvattende aluminawashcoat op een gestructureerde drager is.
14. Werkwijze volgens conclusie 12 of 13, waarbij het product dat gevormd wordt bij de stap waarbij stroom c) in contact wordt gebracht met de gestructureerde drager, wordt toegepast als brandstof voor een gasmotor.

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## UITTREKSEL

De uitvinding heeft betrekking op een werkwijze voor het terugbrengen van het gehalte aan stikstofoxiden in een stikstofoxide- en zuurstofhoudende gasstroom door deze gasstroom in aanwezigheid van een deNOx-katalysator in contact te brengen met een reducerende gasstroom, welke CO, H<sub>2</sub> en eventueel NH<sub>3</sub> omvat en welke reducerende gasstroom is verkregen door koolwaterstoffen om te zetten met de zuurstof uit genoemde stikstofoxide- en zuurstofhoudende gasstroom desgewenst in aanwezigheid van een reductantvormende katalysator.

## P/ NT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

PRINS, A., W.  
Vereenigde  
Nieuwe Parklaan 97  
NL-2587 BN The Hague  
PAYS-BAS

Date of mailing (day/month/year) 08 October 2001 (08.10.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference P48815PC00	
International application No. PCT/NL00/00404	International filing date (day/month/year) 13 June 2000 (13.06.00)

## 1. The following indications appeared on record concerning:

☒ the applicant
 ☒ the inventor
 ☐ the agent
 ☐ the common representative

Name and Address JELLES, Sytse, Jelle Kazernestraat 51 NL-2514 CS Den Haag Netherlands	State of Nationality NL	State of Residence NL
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person
 ☐ the name
 ☒ the address
 ☐ the nationality
 ☐ the residence

Name and Address JELLES, Sytse, Jelle Prins Alexanderstraat 22 NL-8019 XH Zwolle Netherlands	State of Nationality NL	State of Residence NL
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## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Ingrid AULICH
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
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 Arlington, VA 22202  
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 in its capacity as elected Office

Date of mailing (day/month/year) 09 February 2001 (09.02.01)	
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Applicant JELLES, Sytse, Jelle et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

13 December 2000 (13.12.00)

☐ in a notice effecting later election filed with the International Bureau on:
2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38
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(54) Title: METHOD FOR REMOVING NITROGEN OXIDES FROM AN OXYGEN-CONTAINING GAS STREAM

(57) Abstract: A process for removing nitrogen oxides from a gas stream containing nitrogen oxides and oxygen involves bringing the gas stream into contact with a reducing gas stream in the presence of a deNO<sub>x</sub> catalyst. The reducing gas stream contains CO, H<sub>2</sub> and, optionally, NH<sub>3</sub>; it is produced by reacting hydrocarbons with the oxygen from the above mentioned nitrogen oxide- and oxygen-containing gas stream. A catalyst, such as an oxidising or stream-reforming catalyst may be used to promote the reaction which produces the reducing gas stream.

WO 00/76637 A1

Title: Method for removing nitrogen oxides from an oxygen-containing gas stream

This invention relates to a catalytic conversion of nitrogen oxides to molecular nitrogen, which nitrogen oxides are formed upon combustion of hydrocarbons and/or synthesis gas ( $H_2/CO$ ). More particularly, it relates to the conversion of nitrogen oxides in the presence of oxygen such as these are formed, for instance, in the operation of units such as combustion engines under so-called poor or 'lean-burn' conditions, that is: under combustion conditions where an excess of oxygen is present. The invention further relates to the conversion of nitrogen oxides which may be formed in industrial processes, such as nitric acid production.

In the combustion of hydrocarbons with molecular oxygen (for instance originating from air), oxides of nitrogen may be formed due to the prevailing temperature and pressure during the combustion process. These nitrogen oxides, among which  $NO$  and  $NO_2$  (usually denoted by  $NO_x$ ) are very harmful to the environment. Nitrogen oxides are held responsible inter alia for the formation of acid rain and photochemical smog.

Different methods for reducing  $NO_x$  emission are known and a number of them are already being applied in practice.

Reducing  $NO_x$  emission in stoichiometrically running engines is often accomplished by making use of a so-called three-way catalyst system. The  $NO_x$  conversion catalyst in such systems is capable of converting nitrogen oxides to harmless compounds by reacting them with the reducing combustion products present in the exhaust gas, such as hydrocarbons and  $CO$ , to form  $N_2$ .

Generally, the known three-way catalysts which effect the reduction of nitrogen oxides are incapable of performing this conversion in the presence of a considerable amount of oxygen.

This is a problem in particular in the removal of nitrogen oxides from the exhaust gases of the above-mentioned lean-burn engines, such as lean-burn gas turbines, diesel engines, gas engines and off-gases of industrial processes, since in such gases, in addition to nitrogen oxides, a considerable amount of oxygen is present. Moreover, hydrocarbons and/or

CO are not present, or present in an insufficient amount, which is a bar to the successful operation of the above-mentioned three-way catalyst systems.

In installations where a considerable amount of oxygen is present in the exhaust gas, therefore, often an amount of reductant is added. The nitrogen oxides can then be converted by the reductant in the presence of a suitable catalyst (deNO<sub>x</sub> catalyst). This method is known as the so-called Selective Catalytic Reduction (SCR).

Widely used reductants for the SCR reaction are ammonia and urea. Also, it is known from the literature to use hydrocarbons such as ethylene, propylene and propane as reductant (see, for instance, G.P. Ansell *et al.*, 'Mechanism of the lean NO<sub>x</sub> reaction over Cu/ZSM-5', Appl. Catal. B, 2 (1993), pp. 81-100). Other possible reductants are, for instance, CO, H<sub>2</sub> and CH<sub>4</sub>, ethanol, hydrocarbons, in particular fuels such as gasoline and diesel oil.

Used most by far as reductant in practical SCR applications, however, are ammonia or urea, or an aqueous urea solution. The use of these agents entails a number of disadvantages. Dosage is extremely critical. If too large an amount of ammonia or urea is charged to the deNO<sub>x</sub> catalyst (i.e., more than is necessary to convert the nitrogen oxides), this will lead to so-called ammonia slip. The emission of ammonia from such installations is actually even more harmful from an environmental point of view than the emission of NO<sub>x</sub>. Also, it is possible that through oxidation of ammonia, this excess dosage leads to the production of NO<sub>x</sub>, which is the very opposite of the object contemplated, viz. reducing the NO<sub>x</sub> emission. Another disadvantage of the use of ammonia or urea is the necessary storage thereof and the necessity of periodically supplementing the supply if this is not produced within battery limits. In particular ammonia is very dangerous and noxious and the transport thereof involves great safety and environmental risks. As a consequence of all this, both the investment costs and the operational costs of this technique are high.

Although the choice of other reducing agents, such as, for instance, the above-mentioned hydrocarbons, might partly solve these problems, there still remain disadvantages, such as the necessity of separate transport and storage. The attendant safety and environmental hazards are often unacceptable.

This problem would be solved by using as a reducing agent the same fuel that is used or is present in the engine, the (gas) turbine or the combustion process in industrial processes. The hydrocarbons which are present in, for instance, diesel oil and gasoline, however, prove not to be sufficiently active to convert NOx under process conditions with an acceptable rate and selectivity.

It is known to start from an SCR catalyst, with the required reducing agent being manufactured from an available source of hydrocarbons, such as methanol, LPG and natural gas, optionally under addition of H<sub>2</sub> which has been obtained from electrolysis or which is stored in storage tanks.

In DE-A-44 04 617 a technique is described whereby, using an electrically heated reactor, a hydrocarbon-containing fuel is catalytically cracked at 200 to 700°C and the cracking products are further activated with air before they are added as reducing agent to the exhaust gas, whereupon the total gas stream is passed over an SCR catalyst.

According to DE-A-196 00 558, also cracked hydrocarbons are used as reducing agent. These hydrocarbons have been obtained from diesel. According to this known method, under SCR conditions, hydrogen is added to the exhaust gas to reduce NOx over the SCR catalyst where the cracked hydrocarbons are not sufficiently active. The hydrogen originates from a storage tank or is made through electrolysis or methanol reforming.

The addition of hydrogen as reducing agent for the reduction of NOx in the exhaust gases of continuous combustion processes is described in DE-A-42 30 408. There, too, the hydrogen can be obtained by electrolysis or from reforming through steam reforming or partial oxidation (PO) of hydrocarbon containing fuel. To obtain a hydrogen stream with as little carbon monoxide as possible, two shift reactors are placed behind the reformer to convert the CO for the most part with water vapor to form hydrogen and CO<sub>2</sub>.

The use of in situ produced hydrogen as a reducing agent for the reduction of NOx from exhaust gas of internal combustion engines is described in EP-A-0 537 968. In this document, the technique of reforming (steam reforming and partial oxidation) of hydrocarbon containing fuels is described. According to this publication, the conditions must be chosen such

that the amount of CO in the hydrogen is so low that the CO concentration cannot yield any problems regarding emissions. The temperature needed for reforming is achieved by making use of the heat of the exhaust gases. The reduction of NO<sub>x</sub> is carried out over an SCR catalyst. As oxidizing agent for the partial oxidation, air is mentioned.

According to the present invention, in a reductant-forming step, hydrocarbons are converted to a reductant stream under suitable conditions, optionally by contacting them with a reductant forming catalyst. The hydrocarbons in the product stream of the reductant forming step can be unreacted hydrocarbons from the feedstock of this step, but may also be smaller hydrocarbons which have been formed by cracking reactions during the reductant forming step.

The reductants can be prepared, by the use of a reductant forming catalyst, from, for instance, residues of hydrocarbons which are contained in the exhaust gas of the unit in which the combustion takes place. It is also possible to draw these hydrocarbons from a different source, for instance the fuel for the combustion unit, which is already available in situ. Combinations of effluent and such a different source are naturally also possible. The oxygen needed for this step at least partly originates from the off-gas to be treated, i.e., the nitrogen oxide- and oxygen-containing gas. Preferably, substantially all oxygen present in the part of the off-gas used for the reductant formation is used for forming the reducing gas stream. The hydrocarbons present in this portion of the off-gas can also be converted to reducing compounds in this step. The hydrocarbons present in the off-gas can then also be converted to reducing compounds in this step.

Through the use of a suitable reductant forming process, optionally utilizing a catalyst, the reductants necessary for the catalytic reduction of NO<sub>x</sub>, in the form of CO and/or H<sub>2</sub>, optionally supplemented with hydrocarbons, can be prepared from hydrocarbons in situ, so that the above-outlined drawbacks in removing NO<sub>x</sub> under oxygen-rich conditions can be eliminated at least partly.

In addition to the above-mentioned reductants, CO and/or H<sub>2</sub>, optionally supplemented with hydrocarbons, also ammonia (NH<sub>3</sub>) can be formed in the presence of hydrogen and nitrogen, under suitable process

conditions, because of the position of the chemical equilibrium  
 $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$ . As mentioned above, ammonia is a good reductant.

The use of a part of the exhaust gases as a source of hydrocarbons and certainly as an oxidation source for the (catalytic) partial oxidation and/or steam reforming has as a major advantage over the existing technology that the emission of uncombusted hydrocarbons can be minimized, the oxygen content in the total exhaust gas stream decreases, so that the conditions for deNO<sub>x</sub>-ing improve and the energy present in the form of heat in the exhaust gases can be used directly for the catalytic process without making use of extra heat exchanging surface.

Another advantage is that no pure H<sub>2</sub> or H<sub>2</sub> with small amounts of carbon monoxide needs to be produced. As a consequence, it is possible to omit shift reactors and membrane technology.

The reductant forming step can be a partial oxidation step, in which use can be made of a partial oxidation catalyst. In addition, it is possible to carry out the partial oxidation without catalyst, for instance by supplying a controlled amount of energy to a fuel stream, for instance by means of an electrical discharge. Also, the reductant forming step can be a steam reforming step in which use is made of a steam reforming catalyst. A combination of partial oxidation and steam reforming is also possible.

A suitable reductant forming catalyst is, for instance, a partial oxidation catalyst. In the presence of such a catalyst, the partial oxidation of hydrocarbons takes place. As mentioned, according to the invention, the oxygen needed for this partial oxidation is derived from the effluent of the combustion unit, optionally supplemented with oxygen obtained from elsewhere, coming, for instance, from added air. The product stream of the partial oxidation step is highly suitable for use as reductant stream.

Another possibility of preparing a stream comprising H<sub>2</sub> and/or CO, and optionally hydrocarbons, from a stream comprising hydrocarbons, is the use of a so-called steam reforming. In steam reforming, in addition to hydrocarbons, water is to be added to the steam reforming step. This water may originate from the effluent of the combustion engine, from a separate stock, or from a combination of these two sources. In steam reforming, hydrocarbons are converted with water (steam) to a mixture of hydrocarbons, such as methane, and/or H<sub>2</sub> and CO<sub>2</sub>. As a consequence of

chemical equilibria, in addition to these components, CO may also be present. The mixture thus formed is very suitable to be used as a reductant stream.

5 Next, the reductant stream, together with the effluent of the combustion unit, is contacted with a deNOx catalyst so that the desired conversion of nitrogen oxides takes place.

The in situ production of the reductant offers a number of important advantages. Thus, according to the invention, the supply of reductants can take place continuously, in the case of natural gas, or in any case simultaneously with the supply of the fuel for the combustion unit, and it is no longer necessary to have and maintain a separate stock thereof. This can be practical, for instance, when used in mobile combustion units, such as trucks or passenger cars, because then no separate storage tanks for the reducing agent need to be present. This may also be an important  
10 advantage in stationary units. The fact that no ammonia and urea (whether or not as a urea solution) are used, at least do not need to be drawn from elsewhere, is also an advantage because the above-outlined disadvantages associated with the use of these reductants no longer occur.

Another advantage of the invention arises if hydrocarbons from the effluent of the combustion unit are used as feedstock for the reductant forming step, as a result of which the amounts of hydrocarbons in the exhaust gas will then be lowered in that they are used for the reaction with NOx. Such a reduction is favorable, since the emission of hydrocarbons is undesirable from an environmental point of view. Another advantage of the use of the effluent of the combustion unit for the formation of the reducing  
20 gas is the decrease of the amount of hydrocarbons needed for the reductant formation.

Accordingly, the present invention is characterized by a method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing gas stream by contacting this gas stream in the presence of a deNOx catalyst with a reducing gas stream, which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which reducing gas stream has been obtained by converting hydrocarbons with the oxygen from the nitrogen oxide- and oxygen-containing gas stream, optionally in the presence of a reductant forming catalyst.  
30  
35

According to a preferred embodiment, the nitrogen oxide- and oxygen-containing gas stream is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess oxygen with respect to the fuel, which further comprises nitrogen, wherein the effluent, together with the reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with the deNO<sub>x</sub> catalyst, wherein to stream c) no ammonia and no urea is added and wherein stream c) has been substantially obtained by contacting streams d) and e) with the reductant forming catalyst, stream d) comprising one or more hydrocarbons and stream e) comprising oxygen and water.

The combustion unit is suitable for generating heat, and optionally energy. The combustion unit can work on the basis of a flame, but the combustion in the combustion unit can also proceed by catalytic route. Preferably, the combustion unit is a gas engine, gas turbine, diesel engine or gasoline engine.

A stream c) which is substantially free from externally added ammonia and urea is understood to mean that to this stream, in accordance with the invention, no reductants of this type need to be added. Still, ammonia and possibly compounds derived therefrom, such as urea, can be present as a result of the above-mentioned equilibrium reaction of N<sub>2</sub> and H<sub>2</sub>.

According to the present invention, the NO<sub>x</sub> is reduced with a mixture of H<sub>2</sub>, CO and possibly NH<sub>3</sub>. In addition, hydrocarbons which have not been (entirely) converted can be present in the reducing gas stream. These hydrocarbons also work as reductants. The reducing gas mixture is obtained by converting the hydrocarbons from a part of the exhaust gas stream with optionally extra added hydrocarbons, by means of (catalytic) partial oxidation, steam reforming or a combination of both technologies by means of the oxygen and water vapor present in the same part of the exhaust gas stream and optionally externally added air and/or water vapor. Optionally, extra reducing agent such as hydrogen can be added to the reducing gas mixture obtained.

Particularly preferred is the method and the apparatus suitable therefor according to the invention, wherein the engine comprises a heat

exchanger, such that at least a portion of the heat released upon the combustion can be usefully employed, for instance for heating, as of greenhouses or other spaces. Such units, in which at the same time both heat and energy are generated, the energy being typically in the form of electrical power, are also referred to as combined heat and power units or total energy plants.

The invention can also be applied in various means of transport such as vessels, airplanes, trucks and passenger cars and trains provided with a hydrocarbon-fired locomotive engine.

The method according to the invention and the apparatuses suitable therefor is suitable in particular for operating combustion units under so-called lean-burn conditions, i.e., conditions where the ratio between the streams a) and b) is selected such that the amount of oxygen is at least the amount needed for the complete combustion of the fuels in stream a). These are the conditions under which oxygen is present in the effluent of the combustion unit and wherein, with advantage, the deNO<sub>x</sub> reaction with the effluent of the catalytic partial oxidation step can be carried out.

Suitable fuels for the feedstock a) are hydrocarbons and/or synthesis gas (CO/H<sub>2</sub> mixture).

Preferably, the hydrocarbons for the reductant forming step are at least partly drawn from the same source as the fuel for the combustion unit. In this case, stream a) and stream d) comprise the same components.

In order to reduce the content of hydrocarbons in the emission of the apparatus for the method according to the invention, the hydrocarbons that are present in the effluent of the combustion unit are at least partly used as feedstock for the reductant forming step, which may or may not be supplemented with a hydrocarbon stream drawn from elsewhere.

In order to keep the oxygen content low when contacting the streams with the deNO<sub>x</sub> catalyst, the effluent of the combustion unit is used as oxygen source, which may or may not be supplemented with an oxygen stream drawn from elsewhere.

As fuel for the combustion unit and/or as feedstock for the reductant forming step, besides synthesis gas, in principle all hydrocarbons suitable therefor can be used. It is practically preferred, however, when the

hydrocarbons from stream a) and d) are selected independently from the group consisting of natural gas (which comprises substantially methane), methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, derivatives and mixtures thereof.

5       The catalyst for converting nitrogen oxides can be selected from the group of catalysts which catalyze the reduction of NO<sub>x</sub>, such as the conventional catalysts for removal of NO<sub>x</sub>. Preferably, these are selected from the group comprising zeolites, metal-exchanged zeolites, such as Co-, Cu- and/or Ce-exchanged zeolites, Pt, Rh and/or Ir catalyst, optionally  
10       provided on a support such as a washcoat which may further comprise Ba, La, Y, Sr, Pr, Ce, Si, Ti, Al and/or Zr.

      The catalyst for the partial oxidation of hydrocarbons can be selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni, if desired provided on suitable supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>,  
15       silica/alumina-zeolites and mixtures thereof, optionally stabilized with, for instance, Si, La, Ba or Y and mixtures thereof.

      The steam reforming catalyst which is capable of converting a mixture of hydrocarbons and water to a mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and/or hydrocarbons can be any conventional steam reforming catalyst, which may  
20       or may not be supported, according to conventional techniques, as known to the skilled person. Preferably, the steam reforming catalyst is a supported catalyst comprising Ni, Rh and/or Pt.

      For operating an apparatus according to the invention, factors such as hydrocarbon/oxygen ratio, temperature, pressure, residence time and/or  
25       amount of catalyst for the partial oxidation of hydrocarbons should be selected such that no complete oxidation takes place. The molar hydrocarbon/oxygen ratio is expressed in  $\lambda_{PO}$ , such that for stoichiometric ratios (i.e., precisely sufficient oxygen to effect the complete combustion of the fuel),  $\lambda_{PO} = 1$ . According to the invention,  $\lambda_{PO} < 1$ . Preferably,  $0.2 < \lambda_{PO} <$   
30       0.7.  $\lambda_{PO}$  is controllable by adjusting the air/fuel amount and is dependent on the hydrocarbons used.

      The temperature for the reductant forming step is generally between 250 and 1100°C. The residence time for the reductant forming step is generally between 200 en 150,000 h<sup>-1</sup>. Although the pressure will also  
35       have an influence, it is generally dictated by the other process conditions. In

general, the pressure will be atmospheric or slightly higher and not higher than 50 bars.

The use of an SCR catalyst as a method of converting NO<sub>x</sub> with a reducing agent to N<sub>2</sub> often has the limitation that sufficient conversion of NO<sub>x</sub> can be achieved in a limited temperature frame. Thus, in DE-A-196 00 558, as a practical example, a conversion curve of NO<sub>x</sub> as a function of the temperature is given, in which a conversion of 40% is achieved. This is typical of SCR systems that do not work with NH<sub>3</sub> or urea as reducing agent. Selecting the process conditions of the reductant forming step such that also NH<sub>3</sub> is generated is therefore advantageous because then a higher NO<sub>x</sub> conversion can be achieved.

When a high conversion of NO<sub>x</sub> is required, as, for instance, in the application of exhaust gases as fertilizing gas in horticulture, it is better for the method according to the present invention to be carried out with an NO<sub>x</sub> storage system, instead of an SCR system. If the deNO<sub>x</sub> step is carried out with such an NO<sub>x</sub> storage system (also referred to as NO<sub>x</sub> Storage and Reduction Catalyst, NSR), such as described, for instance, in N. Takhashi et al., *Environmental Catalysis*, p. 45, (1995), a very high conversion in NO<sub>x</sub> can be obtained. According to this method, nitrogen oxides are absorbed from the nitrogen oxide- and oxygen-containing gas stream to a suitable absorbent and subsequently, for instance by switching, the reducing gas stream is contacted with the absorbent. The deNO<sub>x</sub> step is thus operated discontinuously. A very effective NO<sub>x</sub> removal can thus be obtained.

With this NO<sub>x</sub> storage system, it is possible to absorb NO<sub>x</sub> in an oxidizing medium ( $\lambda < 1$ ), and in a reducing medium ( $\lambda < 1$ ) to convert both the NO<sub>x</sub> in the exhaust gas and the adsorbed NO<sub>x</sub> to nitrogen. The catalyst in the NO<sub>x</sub> storage system can very suitably consist of platinum provided on a barium-containing and/or zeolite-comprising alumina washcoat. The barium present can react with NO<sub>x</sub> to barium nitrate. This nitrate salt decomposes in a reducing medium to barium and N<sub>2</sub>.

The NO<sub>x</sub> storage system can be operated according to the invention by passing the exhaust gases through the NO<sub>x</sub> storage system until the system is saturated with NO<sub>x</sub>. Thereafter, regeneration can be done with a reducing agent which has been obtained as described above. Optionally, this

reducing agent can be supplemented with a reduction agent drawn from elsewhere.

Preferably, this NO<sub>x</sub> storage system is designed with minimally two parallel beds. One bed is used to absorb NO<sub>x</sub>, while the other bed is regenerated. As soon as the former bed is saturated and/or the second bed is sufficiently regenerated, the streams are switched, so that the regenerated bed can proceed to absorb NO<sub>x</sub> and the loaded NO<sub>x</sub> bed is regenerated in that the absorbed NO<sub>x</sub> is converted to nitrogen.

The effluent of the regeneration step of the NO<sub>x</sub> storage bed can be recirculated with advantage and, together with the inlet air, be passed to the inlet of the combustion unit (for instance a gas engine). This provides at least two advantages. In the first place, in this way no CO-containing gas needs to be discharged. In the second place, according to this embodiment, it is of less importance to obtain a complete conversion of hydrocarbons to CO/H<sub>2</sub> in the preceding preparation step of the reducing gas stream.

Both the deNO<sub>x</sub> catalyst and the reductant forming catalyst can be present in the method according to the invention in the forms known to those skilled in the art, as in the form of a bed of granules, extrusions, granules, and/or pellets, or provided on ceramic or so-called metal monoliths, or differently structured forms.

The use of the catalyst in structured form is preferred because this allows other relevant factors for the method, such as pressure drop, mixing, contact time, heat management, mechanical strength and life, to be tailored to the prevailing conditions through suitable choices, and the method can thereby be optimized.

The invention is therefore characterized by the use of a catalyst suitable for converting nitrogen oxides in combination with either a catalyst suitable for the partial oxidation of hydrocarbons, or a catalyst suitable for steam reforming, for converting nitrogen oxides in generating heat and optionally energy from hydrocarbons, without this requiring ammonia or urea to be added externally.

## CLAIMS

1. A method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing gas stream by contacting this gas stream in the presence of a deNOx catalyst with a reducing gas stream, which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which reducing gas stream has  
5 been obtained by converting hydrocarbons with oxygen and/or water from said nitrogen oxide- and oxygen-containing gas stream, if desired in the presence of a reductant forming catalyst.
2. A method according to claim 1, wherein substantially all of the oxygen present in the part of said nitrogen oxide- and oxygen-containing gas  
10 stream that is used for the reductant formation is used up.
3. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess  
15 oxygen with respect to the fuel; wherein said effluent, together with said reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with said deNOx catalyst; wherein to stream c) no ammonia and no urea is added; and wherein stream c) has been substantially obtained by subjecting streams d) and e) to a reductant  
20 forming step, while stream d) comprises one or more hydrocarbons.
4. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream originates from a combined heat and power unit.
5. A method according to any one of the preceding claims, wherein  
25 said reducing gas stream is obtained by carrying out a partial oxidation step, utilizing a partial oxidation catalyst, or a steam reforming step, utilizing a steam reforming catalyst.
6. A method according to any one of claims 3-5, wherein the fuel in stream a) comprises synthesis gas and/or one or more hydrocarbons.

7. A method according to any one of claims 3-6, wherein stream a) and stream d) comprise at least partly the same compounds.
8. A method according to any one of claims 3-7, wherein the fuel in stream a) comprises hydrocarbons which, like the hydrocarbons in stream d), have been selected independently from the group consisting of natural gas, methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, and mixtures thereof.
9. A method according to any one of the preceding claims, wherein a reductant forming catalyst is used which is a partial oxidation catalyst for the partial oxidation of hydrocarbons, selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni and combinations thereof, optionally provided on a support, which support is optionally stabilized with Si, La, Ba and/or Y.
10. A method according to any one of the preceding claims, wherein the reductant forming catalyst is a steam reforming catalyst which comprises Ni, Rh and/or Pt.
11. A method according to any one of the preceding claims, wherein the reductant forming step is a partial oxidation step, wherein the ratio of hydrocarbons and oxygen is selected such that no complete oxidation takes place.
12. A method according to any one of the preceding claims, wherein nitrogen oxides from the nitrogen oxide- and oxygen-containing gas stream are absorbed onto a suitable absorbent and subsequently said reducing gas stream is contacted with said absorbent.
13. A method according to claim 12, wherein said absorbent is a barium and/or zeolite comprising alumina washcoat on a structured support.
14. A method according to claim 12 or 13, wherein the product that is formed in the step wherein stream c) is contacted with the structured support is used as fuel for a gas engine.

# INTERNATIONAL SEARCH REPORT

Ints. Application No

PCT/NL 00/00404

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01D53/94 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 197 42 705 A (MAZDA MOTOR CORP.) 2 April 1998 (1998-04-02)	1-11
Y	column 3, line 54 -column 4, line 63 ---	12,13
X	EP 0 441 401 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 14 August 1991 (1991-08-14) column 3, line 28 -column 5, line 27 ---	1-9,11
X	DE 196 36 790 A (VOLKSWAGEN AG) 12 March 1998 (1998-03-12) column 8, line 26 -column 9, line 37 ---	1-13
X	WO 98 09699 A (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 12 March 1998 (1998-03-12) page 13, line 15 -page 118, line 13 --- -/--	1-4,6-8, 11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 September 2000

Date of mailing of the international search report

04/10/2000

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/NL 00/00404

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 195 43 219 C (MERCEDES-BENZ AKTIENGESELLSCHAFT) 5 December 1996 (1996-12-05) column 2, line 43 -column 4, line 4	12,13
A	EP 0 537 968 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 21 April 1993 (1993-04-21) column 4, line 32 -column 9, line 18	1-11
A	DE 42 30 408 A (AISIN SEIKI K. K.) 18 March 1993 (1993-03-18) column 4, line 50 -column 6, line 8 column 7, line 65 -column 8, line 34	1-8,10
A	DE 44 04 617 A (DAIMLER-BENZ AKTIENGESELLSCHAFT) 17 August 1995 (1995-08-17) column 1, line 37 -column 2, line 30	1-9,11
A	DE 196 00 558 A (DAIMLER-BENZ AKTIENGESELLSCHAFT) 10 July 1997 (1997-07-10) column 2, line 32 -column 4, line 45	1-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/NL 00/00404

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19742705 A	02-04-1998	JP 10151353 A US 6066587 A	09-06-1998 23-05-2000
EP 441401 A	14-08-1991	JP 2850547 B JP 4214918 A DE 69109315 D DE 69109315 T US 5189876 A	27-01-1999 05-08-1992 08-06-1995 12-10-1995 02-03-1993
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DE 4230408 A	18-03-1993	JP 5071334 A NL 9201586 A US 5441401 A	23-03-1993 01-04-1993 15-08-1995
DE 4404617 A	17-08-1995	US 5586433 A	24-12-1996
DE 19600558 A	10-07-1997	EP 0783918 A US 5921076 A	16-07-1997 13-07-1999

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P48815PC00</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/NL 00/ 00404</b>	International filing date (day/month/year) <b>13/06/2000</b>	(Earliest) Priority Date (day/month/year) <b>11/06/1999</b>
Applicant <b>GASTEC N.V. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.  
☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/NL 00/00404

## Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

A process for removing nitrogen oxides from a gas stream containing nitrogen oxides and oxygen involves bringing the gas stream into contact with a reducing gas stream in the presence of a deNOX catalyst. The reducing gas stream contains CO, H<sub>2</sub> and, optionally, NH<sub>3</sub>; it is produced by reacting hydrocarbons with the oxygen from the above mentioned nitrogen oxide- and oxygen-containing gas stream. A catalyst, such as an oxidising or steam-reforming catalyst may be used to promote the reaction which produces the reducing gas stream

**REPLACED BY  
ART 34 AMDT**

## CLAIMS

1. A method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing gas stream by contacting this gas stream in the presence of a deNO<sub>x</sub> catalyst with a reducing gas stream, which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which reducing gas stream has  
5 been obtained by converting hydrocarbons with oxygen and/or water from said nitrogen oxide- and oxygen-containing gas stream, if desired in the presence of a reductant forming catalyst.
2. A method according to claim 1, wherein substantially all of the oxygen present in the part of said nitrogen oxide- and oxygen-containing gas  
10 stream that is used for the reductant formation is used up.
3. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess  
15 oxygen with respect to the fuel; wherein said effluent, together with said reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with said deNO<sub>x</sub> catalyst; wherein to stream c) no ammonia and no urea is added; and wherein stream c) has been substantially obtained by subjecting streams d) and e) to a reductant  
20 forming step, while stream d) comprises one or more hydrocarbons.
4. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream originates from a combined heat and power unit.
5. A method according to any one of the preceding claims, wherein  
25 said reducing gas stream is obtained by carrying out a partial oxidation step, utilizing a partial oxidation catalyst, or a steam reforming step, utilizing a steam reforming catalyst.
6. A method according to any one of claims 3-5, wherein the fuel in stream a) comprises synthesis gas and/or one or more hydrocarbons.

7. A method according to any one of claims 3-6, wherein stream a) and stream d) comprise at least partly the same compounds.
8. A method according to any one of claims 3-7, wherein the fuel in stream a) comprises hydrocarbons which, like the hydrocarbons in stream d), have been selected independently from the group consisting of natural gas, methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, and mixtures thereof.
9. A method according to any one of the preceding claims, wherein a reductant forming catalyst is used which is a partial oxidation catalyst for the partial oxidation of hydrocarbons, selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni and combinations thereof, optionally provided on a support, which support is optionally stabilized with Si, La, Ba and/or Y.
10. A method according to any one of the preceding claims, wherein the reductant forming catalyst is a steam reforming catalyst which comprises Ni, Rh and/or Pt.
11. A method according to any one of the preceding claims, wherein the reductant forming step is a partial oxidation step, wherein the ratio of hydrocarbons and oxygen is selected such that no complete oxidation takes place.
12. A method according to any one of the preceding claims, wherein nitrogen oxides from the nitrogen oxide- and oxygen-containing gas stream are absorbed onto a suitable absorbent and subsequently said reducing gas stream is contacted with said absorbent.
13. A method according to claim 12, wherein said absorbent is a barium and/or zeolite comprising alumina washcoat on a structured support.
14. A method according to claim 12 or 13, wherein the product that is formed in the step wherein stream c) is contacted with the structured support is used as fuel for a gas engine.

PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT



(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P48815PC00	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL00/00404	International filing date (day/month/year) 13/06/2000	Priority date (day/month/year) 11/06/1999
International Patent Classification (IPC) or national classification and IPC B01D53/94		
Applicant GASTEC N.V. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
  - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the report
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  13/12/2000	Date of completion of this report  31.07.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  De Waha, R  Telephone No. +49 89 2399 8306  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/NL00/00404

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-11 as originally filed

**Claims, No.:**

1-13 as received on 28/06/2001 with letter of 28/06/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/NL00/00404

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	1-13
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-13
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**ITEM V**

**NOVELTY, INVENTIVE STEP and INDUSTRIAL APPLICABILITY**

Claim 1 is directed to a method for reducing nitrogen oxides in an effluent gas which comprises (optional features disregarded)

- feeding a stream c to the effluent gas stream
- and contacting this resulting stream with a denox catalyst
- stream c originating from contacting
  - \* a first stream d (being a hydrocarbon stream in totality from a different source than the effluent OR being a hydrocarbon stream consisting partly from effluent stream and partly from a different source, but NOT from pure effluent stream) with a
  - \* second stream e from the effluent stream containing excess oxygen and /or water
  - \* all of the oxygen present in the part of the effluent gas for the formation of the reductant gas stream c being used up.

It is noted that under the EPC and under a number of national laws, the expression used in claim1 "SUBSTANTIALY all of the oxygen ... is used up" is considered unclear. The scope of the claim would be clear by using the expression of page 4 lines 21/22 without the expression "substantially".

**1. NOVELTY**

None of the prior art discloses a method where a hydrocarbon stream from a non-effluent stream or containing a partly effluent/partly non-effluent hydrocarbon stream is contacted with an oxygen and/or water containing effluent stream in such a way that the remaining oxygen from the effluent steam is used up and subsequently contacting this resulting stream c with the effluent stream in the presence of a denox catalyst.

The subject-matter of claim 1 and the subject-matter of the dependant claims therefore appears to be novel (R 33(2) PCT).

## **2. INVENTIVE STEP**

The closest prior art is described in EP 0 441 401 which relates to the off gas treatment of a lean burning diesel engine which involves treating the off gas with a cracked hydrocarbon stream to reach low NO<sub>x</sub> concentrations.

The distinguishing feature lies in the fact that the invention uses a stream obtained by combining an external hydrocarbon stream with part of the off gas stream (to give a reducing gas stream without any residual oxygen) and feed this stream, together with the effluent, to the denox catalyst and to subsequently reach low NO<sub>x</sub> levels.

The prior art gives no incentive to use this procedure.

The problem solved is to provide another (alternative) off gas treatment process.

It appears that the application involves an inventive step (R 33(3) PCT).

## **3. INDUSTRIAL APPLICABILITY**

The invention is industrially applicable.

EPO - DG 1

28. 06. 2001

Amended claims

(41)

1. A method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing effluent by contacting this effluent in the presence of a deNOx catalyst, optionally in a NOx-storage system, with a reducing gas stream c), which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which  
5 stream c) has been obtained by converting a stream d), which comprises one or more hydrocarbons which are at least partly drawn from a different source than said effluent, with a stream e) comprising oxygen and/or water from said effluent stream, if desired in the presence of a reductant forming catalyst, wherein substantially all of the oxygen present in stream e) that is used for the  
10 formation of stream c) is used up.
2. A method according to claim 1, wherein said effluent is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess oxygen with respect to the fuel; wherein said effluent, together with said  
15 reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with said deNOx catalyst; wherein to stream c) no ammonia and no urea is added.
3. A method according to any one of the preceding claims, wherein said effluent originates from a combined heat and power unit.
- 20 4. A method according to any one of the preceding claims, wherein said stream c) is obtained by carrying out a partial oxidation step, utilizing a partial oxidation catalyst, or a steam reforming step, utilizing a steam reforming catalyst.
5. A method according to any one of claims 2-4, wherein the fuel in  
25 stream a) comprises synthesis gas and/or one or more hydrocarbons.
6. A method according to any one of claims 2-5, wherein stream a) and stream d) comprise at least partly the same compounds.

7. A method according to any one of claims 2-6, wherein the fuel in stream a) comprises hydrocarbons which, like the hydrocarbons in stream d), have been selected independently from the group consisting of natural gas, methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, and mixtures thereof.
8. A method according to any one of the preceding claims, wherein a reductant forming catalyst is used which is a partial oxidation catalyst for the partial oxidation of hydrocarbons, selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni and combinations thereof, optionally provided on a support, which support is optionally stabilized with Si, La, Ba and/or Y.
9. A method according to any one of the preceding claims, wherein the reductant forming catalyst is a steam reforming catalyst which comprises Ni, Rh and/or Pt.
10. A method according to any one of the preceding claims, wherein the reductant forming step is a partial oxidation step, wherein the ratio of hydrocarbons and oxygen is selected such that no complete oxidation takes place.
11. A method according to any one of the preceding claims, wherein nitrogen oxides from said effluent are absorbed onto a suitable absorbent and subsequently said reducing gas stream is contacted with said absorbent.
12. A method according to claim 11, wherein said absorbent is a barium and/or zeolite comprising alumina washcoat on a structured support.
13. A method according to claim 11 or 12, wherein the product that is formed in the step wherein stream c) is contacted with the structured support is used as fuel for a gas engine.

## Amended claims

1. A method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing effluent by contacting this effluent in the presence of a deNO<sub>x</sub> catalyst, optionally in a NO<sub>x</sub>-storage system, with a reducing gas stream c), which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which  
5 stream c) has been obtained by converting a stream d), which comprises one or more hydrocarbons which are at least partly drawn from a different source than said effluent, with a stream e) comprising oxygen and/or water from said effluent stream, if desired in the presence of a reductant forming catalyst, wherein substantially all of the oxygen present in stream e) that is used for the  
10 formation of stream c) is used up.
2. A method according to claim 1, wherein said effluent is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess oxygen with respect to the fuel; wherein said effluent, together with said  
15 reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with said deNO<sub>x</sub> catalyst; wherein to stream c) no ammonia and no urea is added.
3. A method according to any one of the preceding claims, wherein said effluent originates from a combined heat and power unit.
- 20 4. A method according to any one of the preceding claims, wherein said stream c) is obtained by carrying out a partial oxidation step, utilizing a partial oxidation catalyst, or a steam reforming step, utilizing a steam reforming catalyst.
5. A method according to any one of claims 2-4, wherein the fuel in  
25 stream a) comprises synthesis gas and/or one or more hydrocarbons.
6. A method according to any one of claims 2-5, wherein stream a) and stream d) comprise at least partly the same compounds.

7. A method according to any one of claims 2-6, wherein the fuel in stream a) comprises hydrocarbons which, like the hydrocarbons in stream d), have been selected independently from the group consisting of natural gas, methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, and mixtures thereof.
8. A method according to any one of the preceding claims, wherein a reductant forming catalyst is used which is a partial oxidation catalyst for the partial oxidation of hydrocarbons, selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni and combinations thereof, optionally provided on a support, which support is optionally stabilized with Si, La, Ba and/or Y.
9. A method according to any one of the preceding claims, wherein the reductant forming catalyst is a steam reforming catalyst which comprises Ni, Rh and/or Pt.
10. A method according to any one of the preceding claims, wherein the reductant forming step is a partial oxidation step, wherein the ratio of hydrocarbons and oxygen is selected such that no complete oxidation takes place.
11. A method according to any one of the preceding claims, wherein nitrogen oxides from said effluent are absorbed onto a suitable absorbent and subsequently said reducing gas stream is contacted with said absorbent.
12. A method according to claim 11, wherein said absorbent is a barium and/or zeolite comprising alumina washcoat on a structured support.
13. A method according to claim 11 or 12, wherein the product that is formed in the step wherein stream c) is contacted with the structured support is used as fuel for a gas engine.